BULLETIN
DE
L'ACADÉMIE POLONAISE DES SCIENCES

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VOLUME II
NUMÉRO 5

VARSOVIE 1954

PRINTED IN POLAND

PAŃSTWOWE WYDAWNICTWO NAUKOWE — WARSZAWA 1954

Nakład 1019 + 100 egz.	*Rękopis dostarczono 22. IV. 1954*
Ark. wyd. 3·1, druk. $3^3/_{16}$	*Podpisano do druku 9. VI. 1954*
Papier bezdrzewny sat. 80 g kl. III	*Druk ukończono 15. VI. 1954*
Format B 5, 70×100 cm	*Zam. prod. 223/54 Cena zł 5,—*

KRAKOWSKA DRUKARNIA NAUKOWA, KRAKÓW, UL. CZAPSKICH 4

BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

MATHÉMATIQUE

Sur un problème de J. F. Pál sur les courbes continues

par

K. URBANIK

Présenté par K. BORSUK à la séance du 25 Janvier 1954

Le théorème qui suit est la solution du problème posé par J. F. Pál et publié plusieurs années après sa mort par S. Bundgaard [1].

Théorème. *Une courbe continue* $x(t)$, *où* $0 \leqslant t \leqslant 1$, *assujettie à la condition*

$$x(0) \neq x(1) \tag{1}$$

étant donnée dans un espace métrique $\mathfrak{X}$, *il existe pour tout* $n = 1,2,\ldots$ *un système de nombres*

$$0 = t_0 < t_1 < t_2 < \ldots < t_n < t_{n+1} = 1 \tag{2}$$

tel que

$$\varrho[x(t_{i-1}), x(t_i)] = \varrho[x(t_i), x(t_{i+1})] \quad \textit{pour tout} \quad i = 1,2,\ldots,n \tag{3}$$

(ϱ *désignant la distance dans* $\mathfrak{X}$).

La condition (1) est une hypothèse essentielle, comme le montre, pour n pairs, l'exemple dans lequel $\mathfrak{X}$ est l'ensemble des nombres réels et

$$x(t) = \begin{cases} 2t & \text{pour} \quad 0 \leqslant t \leqslant 1/2, \\ 2-2t & \text{pour} \quad 1/2 \leqslant t \leqslant 1. \end{cases}$$

Il existe des exemples analogues parmi les courbes simples fermées lorsque $\mathfrak{X}$ est le plan. J'en dois ceux pour n impairs à J. Łukaszewicz.

La démonstration du théorème sera basée sur un lemme concernant les simplexes géométriques.

Notations. Étant donné dans l'espace euclidien à n dimensions un système de $n+1$ points $p_0,\ldots,p_n$ linéairement indépendants, $S = p_0,\ldots,p_n$ désignera le simplexe (fermé) ayant ces points pour sommets, c'est-à-dire l'ensemble des points p de la forme $p = \lambda_0 p_0 + \ldots + \lambda_n p_n$ (en notation vectorielle) où $\lambda_0 + \ldots + \lambda_n = 1$ et $\lambda_i \geqslant 0$ pour $i = 0,\ldots,n$. $\dot{S}$ désignera sa frontière et Q_i sa face opposée au sommet p_i, c'est-à-dire l'ensemble des points

pour lesquels on a $\lambda_i = 0$. Évidemment

$$Q_0 + \ldots + Q_n = \dot{S} \tag{4}$$

et

$$Q_0 \cdot \ldots \cdot Q = 0. \tag{5}$$

Lemme. *Soit f une transformation continue du simplexe S telle que*

$$f(Q_i) \subset Q_i. \qquad i = 0, \ldots, n \tag{6}$$

On a alors $S \subset f(S)$.

Démonstration. D'après un théorème général, si les ensembles fermés $F_0, \ldots, F_n$ satisfont aux conditions

$$F_0 + \ldots + F_n = S \tag{7}$$

et

$$Q_i \subset F_i, \tag{8}$$

on a

$$F_0 \cdot \ldots \cdot F_n \neq 0 \tag{9}$$

(p. ex. [2], p. 194, théor. 6, cas des ensembles A_i ouverts; [3]).

Or, en supposant que le lemme est en défaut, soit q un point intérieur de S tel que $q \in S - f(S)$ et soit $g(p)$ la projection du point $f(p)$ sur $\dot{S}$ effectuée du point q; g est donc une transformation continue du simplexe S et $g(S) \subset \dot{S}$. Par conséquent, les ensembles

$$F_i = g^{-1}(Q_i) \qquad i = 0, \ldots, n \tag{10}$$

sont fermés.

Nous allons montrer que les formules (7) et (8) sont satisfaites, tandis que la formule (9) ne l'est pas (ce qui achevera la démonstration du lemme). On a en effet, d'après (10) et (4)

$$F_0 = \ldots + F_n = g^{-1}(Q_0 + \ldots + Q_n) = g^{-1}(\dot{S}) = S.$$

D'autre part, si $p \in Q_i$, on a d'après (6), $f(p) \in Q_i$, d'où $g(p) = f(p)$, donc $g(p) \in Q_i$, c'est-à-dire $p \in g^{-1}(Q_i) = F_i$. L'inclusion (8) est donc établie.

Finalement, il vient d'après (10) et (5)

$$F_0 \cdot \ldots \cdot F_n = g^{-1}(Q_0) \cdot \ldots \cdot g^{-1}(Q_n) = g^{-1}(Q_0 \cdot \ldots \cdot Q_n) = 0.$$

Démonstration du théorème. Définissons comme suit la fonction continue f transformant S en $f(S) \subset S$: pour tout point $p = \lambda_0 p_0 + \ldots + \lambda_n p_n$ soit

$$f(p) = f_0(p)\, p_0 + \ldots + f_n(p)\, p_n$$

où

$$f_i(p) = \frac{\varrho[x(t_i), x(t_{i+1})]}{\sum_{j=0}^{n} \varrho[x(t_j), x(t_{j+1})]} \tag{11}$$

et

$$t_0 = 0 \quad \text{et} \quad t_{i+1} = \lambda_0 + \ldots + \lambda_i \qquad i = 0, \ldots, n \tag{12}$$

Le dénominateur dans (11) est au moins égal à $\varrho[x(0), x(1)]$, donc non nul en vertu de (1). En même temps, $\lambda_i = 0$ entraîne $t_{i+1} = t_i$, donc $f_i(p) = 0$ d'après (11); on a donc (6). Il en résulte en vertu du lemme que $f(S)$ contient en particulier le barycentre $f(p)$ de S. Comme on a pour celui-ci $f_0(p) = \ldots = f_n(p)$, les nombres (12) déterminés par ces égalités constituent bien un système (2) qui satisfait à (3) en vertu de (11). L'existence d'un tel système est ainsi établie.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

MATHEMATICS

A Definition of the Notion of Distribution

by
R. SIKORSKI

Presented by K. KURATOWSKI on April 2, 1954

The purpose of this paper is to give a definition of distribution, which seems to be more natural than the original definition of L. Schwartz [3]. The present definition has the advantage of making it directly evident that each distribution on each compact (i. e. closed and bounded) interval is a derivative (of a finite order) of a continuous function, and that each distribution on an open interval is locally a derivative (of a finite order) of a continuous function. The main idea of this definition is similar to that of König's [1] definition. For simplicity we shall consider only the one-dimensional case. However, it will be obvious what modifications are necessary to obtain the definition in the k-dimensional case, $k > 1$.

$C(Z)$ will denote the set of all continuous complex functions defined on a set Z.

Let P be a compact interval and let V_n $(n = 0, 1.2, \dots)$ be the set of all polynomials (considered as functions on P only) of degree $< n$. In particular, V_0 contains only the function equal identically to zero. Consider the set of all pairs $\{n. f\}$ where $n = 0, 1, 2, \dots$ and $f \in C(P)$. We write

$$\{n, f\} = \{m, g\} \qquad (n \geqslant m) \tag{1}$$

if f has the continuous derivative $f^{(n-m)}$ of order $n - m$, and $f^{(n-m)} - g \in V_m$. The pairs $\{n, f\}$ (more exactly, the classes of abstraction with respect to the equivalence relation (1)) are called *distribution on the closed interval* P and will be denoted by the letter Θ with indices. If $\Theta = \{n, f\}$, then $\{n, f\}$ is said to be a representative of Θ of degree n. Of course, if Θ has a representative of degree n, it also has a representative of each degree $\geqslant n$. The class D_P of all distributions on P is a linear space with the following definition of operations:

$$\{n, f\} + \{n, g\} = \{n, f + g\}, \qquad c \cdot \{n, f\} = \{n, cf\}. \tag{2}$$

The derivative Θ' (denoted also by $\mathbf{D}(\Theta)$) of a distribution $\Theta = \{n, f\}$ is the distribution

$$\Theta' = \mathbf{D}(\Theta) = \{n, f\}' = \{n + 1, f\}. \tag{3}$$

Now we identify each function $f \in C(P)$ with the distribution $\{0, f\}$. More generally, if f is a function integrable on P and g is its indefinite integral, we identify f with the distribution $\{1, g\}$. Of course, the usual operations $f+g$, cf and (for absolutely continuous functions) f' coincide, after this identification, with the operations defined by (2) and (3). If $\Theta = \{n, f\}$, then, by the above identification, $\Theta = \{0, f\}^{(n)} = \mathbf{D}^n(f)$, i. e. Θ is the n^{th} derivative (in the sense defined by (3)) of the function f.

The neighbourhood (or sequential) topology in D_P is the strongest topology such that 1^0 the imbedding of the space $C(P)$ (with the usual topology) in D_P is continuous, 2^0 the operation $\mathbf{D}$ of derivation is continuous. In particular $\Theta_n \to \Theta$ if and only if there exist representatives $\{m, f_n\} = \Theta_n$ and $\{m, f\} = \Theta$ of the same degree m, such that $f_n \to f$ uniformly on P.

Let P_0 be a closed interval, $P_0 \subset P$. If $\Theta = \{n, f\} \in D_P$, then $\Theta | P_0$ denotes the distribution $\{n, f|P_0\} \in D_{P_0}$, where $f|P_0$ is the function f restricted to P_0. Clearly the projection $\pi_{P,P_0}(\Theta) = \Theta|P_0$ of D_P onto D_{P_0} is a continuous linear operation, and $\pi_{P,P_0}\big(\mathbf{D}(\Theta)\big) = \mathbf{D}\big(\pi_{P,P_0}(\Theta)\big)$.

Now let Q be an open (bounded or not) interval. Consider all the infinite sequences

$$\vartheta = \{\Theta_1, \Theta_2, \Theta_3, \dots\}, \tag{4}$$

where $\Theta_n \in D_{P_n}$, $\{P_n\}$ is an increasing sequence of compact intervals, $Q = P_1 + P_2 + , \dots$ and $\Theta_n = \Theta_{n+1}|P_n$ for $n = 1, 2, \dots$ If

$$\vartheta^* = \{\Theta_1^*, \Theta_2^*, \Theta_3^*, \dots\}$$

is another sequence of this type (i. e. $\Theta_n^* \in D_{P_n^*}$, $\{P_n^*\}$ is an increasing sequence of compact intervals, $Q = P_1^* + P_2^* + , \dots$ and $\Theta_n^* = \Theta_{n+1}^*|P_n^*$ for $n = 1, 2, \dots$), then we write

$$\vartheta = \vartheta^* \tag{5}$$

if an only if $\Theta_n|P_nP_m^* = \Theta_n^*|P_nP_m^*$ for $n, m = 1, 2, \dots$

The sequences (4) (more exactly, the classes of abstraction with respect to the equivalence relation (5)) are called the *distributions on the open interval* Q. The set of all distributions on Q will be denoted by D_Q^*. In the sequel we shall write all distributions $\vartheta \in D_Q^*$ in the form (4), where $\{P_n\}$ is a fixed sequence of intervals.

D_Q^* is a linear space with the operations

$$\{\Theta_1, \Theta_2, \Theta_3, \dots\} + \{\Theta_1^*, \Theta_2^*, \Theta_3^*, \dots\} = \{\Theta_1 + \Theta_1^*, \Theta_2 + \Theta_2^*, \Theta_3 + \Theta_3^*, \dots\}, \tag{6}$$

$$c \cdot \{\Theta_1, \Theta_2, \Theta_3, \dots\} = \{c\Theta_1, c\Theta_2, c\Theta_3, \dots\}. \tag{7}$$

The definition of the derivative $\vartheta' = \mathbf{D}(\vartheta)$ of a distribution $\vartheta \in D_Q^*$ of the form (4) is as follows

$$\mathbf{D}(\vartheta) = \vartheta' = \{\Theta_2', \Theta_3', \Theta_4', \dots\}. \tag{8}$$

If $\Theta_n = \{0, f|P_n\}$ for $n = 1, 2, \dots$, where $f \in C(Q)$, we identify the distribution (4) with the function f. More generally, if f is a locally integrable

function on Q and g is its indefinite integral, then we identify f with the distribution (4), where $\Theta_n = \{1, g \mid P_n\}$ for $n = 1, 2, \ldots$ The usual operations $f+g$, cf and f' coincide, after this identification, with the operations defined by (6), (7), (8).

If $\vartheta \in D_Q^*$ is of the form (4) and if $P \subset Q$ is a compact interval, then $\vartheta \mid P$ is the distribution $\Theta_n \mid P$, where n is such an integer, that $P \subset P_n$.

The topology in D_Q^* is the weakest topology such that all projections $\pi_{Q,P}(\vartheta) = \vartheta \mid P$ (where $P \subset Q$ is a compact interval) are continuous.

The correspondence $\vartheta \leftrightarrow T_\vartheta$ between distributions $\vartheta \in D_Q^*$ (of the form (4)) and Schwartz's functionals T defined on the space of all infinitely differentiable functions φ on Q with compact carriers, is given by the formula

$$T(\varphi) = (-1)^m \int_{P_n} f \varphi^{(m)} \, dx,$$

where n is such an integer that P_n contains the carrier of φ, and $\Theta_n = \{m, f\}$.

The space of all distributions on a compact interval P can be defined axiomatically as follows: it is an ordered system $\langle D_P, C_P, h_P, \mathbf{D} \rangle$ such that:

(i) D_P is a complex linear topological space;

(ii) C_P is a linear subspace of D_P;

(iii) h_P is a one-to-one linear transformation of $C(P)$ onto C_P;

(iv) $\mathbf{D}$ is a linear transformation of D_P into itself;

(v) $\mathbf{D}^n\big(h_P(f)\big) = \mathbf{D}^m\big(h_P(g)\big)$ (where $n \geqslant m$, $f, g \in C(P)$) if and only if $f^{(n-m)} - g \in V_m$;

(vi) for each $\Theta \in D_P$ there exist an integer $n \geqslant 0$ and a function $f \in C(P)$ such that $\Theta = \mathbf{D}^n\big(h_P(f)\big)$;

(vii) the topology in D_P is the strongest topology such that h_P and $\mathbf{D}$ are continuous.

It follows directly from this axiomatic definition that, for every closed interval $P_0 \subset P$, there is exactly one continuous linear transformation π_{P,P_0} of D_P onto D_{P_0} such that

$$\pi_{P,P_0}\big(\mathbf{D}(\Theta)\big) = \mathbf{D}\big(\pi_{P,P_0}(\Theta)\big), \qquad \pi_{P,P_0}\big(h_P(f)\big) = h_{P_0}(f \mid P_0).$$

The space of all distributions on an open interval Q can be defined as the limit space of the inverse mapping system (see e. g. Lefschetz [2]) $\langle \{D_P\}, \{\pi_{P,P_0}\} \rangle$, where P, P_0 run over the class of all compact subintervals of Q and $P_0 \subset P$.

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POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

THEORETICAL PHYSICS

Classical Properties of Oscillator Wave Packets

by

J. PLEBAŃSKI

Presented by W. RUBINOWICZ on February 22, 1954

1. It was shown long ago [1] that, in the case of a harmonic oscillator, if we take as initial condition the general Gauss function, we obtain a wave packet with classical properties: the packet centrum moves according to classical mechanics; the mean squared error of position (which simultaneously measures the packet width) is a simple periodical time function.

In this paper*) it will be shown that the properties of a Kennard packet are consequences of some general classical properties which are valid for all time-depending wave functions of the oscillator. Using these general properties which are found for all solutions of the wave equation, we obtain a certain special family of wave packets. These packets, being in close correlation with stationary states, have classical properties very similar to the properties of a Kennard packet. Throughout the whole paper the ket notation will be used [2].

2. Let x, p, ω be the position, momentum and cyclic frequency respectively of the oscillator (with mass m). Let us use dimensionless quantities, $\xi \overset{\text{df}}{=} (m\omega/\hbar)^{1/2} x, \eta \overset{\text{df}}{=} (m\omega\hbar)^{-1/2} p, \tau \overset{\text{df}}{=} \omega t$. The ξ and η satisfy therefore $[\eta, \xi] = -i$; their normalised eigenkets will be noted as $|\xi'\rangle, |\eta'\rangle$. In this notation the oscillator state vector $|\psi(\tau)\rangle$ we obtain from initial state $|\psi_0\rangle$ as: $|\psi(\tau)\rangle = e^{i\tau H}|\psi_0\rangle$, where $H \overset{\text{df}}{=} 1/2(\eta^2 + \xi^2)$. The H has a complete ortonormal set of eigenkets $|n'\rangle$ (also $H|n'\rangle = (n' + 1/2)|n'\rangle$), the phases of which can be so chosen that their representations in the position and momentum spaces are given by:

$$\text{(1 a)} \quad q_{n'}(\xi') \overset{\text{df}}{=} \langle \xi' | n' \rangle = u_{n'}(\xi') i^{n'/2} \qquad \text{(1 b)} \quad p_{n'}(\eta') \overset{\text{df}}{=} \langle \eta' | n' \rangle = u_{n'}(\eta') i^{-n'/2}$$

where

$$u_n(a) \overset{\text{df}}{=} \pi^{-1/4} (2^n n!)^{-1/2} H_n(a) e^{-a^2/2}.$$

*) A more extensive paper, containing all the formulae, together with detailed proofs, will be published in Acta Phys. Pol.

Let us introduce the following unitary operator:

$$\Omega(\xi_0, \eta_0) \overset{\text{df}}{=} e^{-i\xi_0\eta_0/2} \cdot e^{i\eta_0\xi} \cdot e^{-i\xi_0\eta} \equiv e^{i\xi_0\eta_0/2} \cdot e^{-i\xi_0\eta} \cdot e^{i\eta_0\xi} \text{ *)}. \tag{2}$$

It can be shown that

$$e^{-itH}\, \Omega(\xi_0, \eta_0)\, e^{itH} = \Omega[\bar{\xi}(\tau), \bar{\eta}(\tau)], \tag{3 a}$$

where

$$\bar{\xi}(\tau) \overset{\text{df}}{=} \xi_0 \cos\tau + \eta_0 \sin\tau, \tag{3 b}$$

$$\bar{\eta}(\tau) \overset{\text{df}}{=} -\xi_0 \sin\tau + \eta_0 \cos\tau. \tag{3 c}$$

The $\bar{\xi}$, $\bar{\eta}$ functions are also solutions of classical equations of motion, with initial conditions ξ_0, η_0 $\left(\text{i. e. } \frac{d}{d\tau}\bar{\xi} = \bar{\eta},\ \frac{d}{d\tau}\bar{\eta}, = -\bar{\xi}\right)$. Let us now introduce an operator $\Pi(a)$ (a is a positive number), which is defined by

$$\Pi(a)\,|\xi'\rangle \overset{\text{df}}{=} a^{1/2}\,|\xi''\rangle;\ \xi'' = a\xi' \text{ **)}. \tag{4}$$

It can be proved that:

$$e^{-itH}\Pi(a) \equiv e^{1/2\xi^2 \frac{d}{d\tau}\log b(\tau)}\, \Pi[b(\tau)]\, e^{-iH\operatorname{arctg} a^{-2}\operatorname{tg}\tau} \equiv e^{i/2\eta^2 \frac{d}{d\tau}\log c(\tau)}\, \Pi[c(\tau)]\, e^{-iH\operatorname{arctg} a^2\operatorname{tg}\tau}, \tag{5a}$$

where

$$b(\tau) \overset{\text{df}}{=} (a^2\cos^2\tau + a^{-2}\sin^2\tau)^{1/2}, \tag{5 b}$$

$$c(\tau) \overset{\text{df}}{=} (a^{-2}\cos^2\tau + a^2\sin^2\tau)^{1/2}. \tag{5 c}$$

Now let the probability amplitudes in the position and momentum spaces: $Q(\xi', \tau) \overset{\text{df}}{=} \langle\xi'|e^{itH}|\Psi_0\rangle$, $P(\eta', \tau) \overset{\text{df}}{=} \langle\eta'|e^{itH}|\Psi_0\rangle$ correspond with the initial state $|\Psi_0\rangle$. We assume these functions to be known. We can then easily give probability amplitudes $\bar{Q}(\xi', \tau)$, $\bar{P}(\eta', \tau)$, corresponding to the initial state $|\bar{\Psi}_0\rangle = \Omega(\xi_0, \eta_0)\, \Pi(a)\, |\Psi_0\rangle$. Using (3 a—5 a—4—2), we find that:

$$\bar{Q}(\xi', \tau) \overset{\text{df}}{=} \langle\xi'|e^{-itH}|\bar{\Psi}_0\rangle = b^{-1/2}(\tau) \cdot Q[\{\xi' - \bar{\xi}(\tau)\}/b(\tau), \operatorname{arctg} a^{-2}\operatorname{tg}\tau] \times$$
$$\times \exp i[\xi'\,\bar{\eta}(\tau) - \bar{w}(\tau) + 1/2\,\{\xi' - \bar{\xi}(\tau)\}^2\, d/d\tau \log b(\tau) - \xi_0\eta_0/2], \tag{6 a}$$

$$\bar{P}(\eta', \tau) \overset{\text{df}}{=} \langle\eta'|e^{-itH}|\bar{\Psi}_0\rangle = c^{-1/2}(\tau) P[\{\eta' - \bar{\eta}(\tau)\}/c(\tau), \operatorname{arctg} a^2\operatorname{tg}\tau] \times$$
$$\times \exp i[-\bar{\eta}'\,\bar{\xi}(\tau) + \bar{w}(\tau) + 1/2\,\{\eta' - \bar{\eta}(\tau)\}^2\, d/d\tau \log c(\tau) + \xi_0\,\eta_0/2], \tag{6 b}$$

where $\bar{\xi}$, $\bar{\eta}$ are given by (3 b—3 c), $b(\tau)$ and $c(\tau)$ by (5 b—5 c), and $\bar{w}(\tau) \overset{\text{df}}{=} 1/2(\bar{\xi}(\tau)\bar{\eta}(\tau) - \xi_0\eta_0)$ has the meaning of classical action correlated with classical motion $\bar{\xi}(\tau)$, $\bar{\eta}(\tau)$.

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*) The ξ_0 and η_0 are numbers. Proof of their identity can be given most easily through the computation matrix elements of both sides in position representation (taking into consideration that $\eta = -i\,\partial/\partial\xi$.

**) It can be easily shown that $\Pi(a)$ is unitary.

If $Q(\xi', \tau)$ is a solution of the Schrödinger equation (in ξ representation) then $\overline{Q}(\xi', \tau)$ from (6 a) is another solution of this equation with arbitrary values of the parameters a, ξ_0, η_0. This can also be proved directly by the substitution of $\overline{Q}$ in the Schrödinger equation. It is also easily shown that $\overline{P}$ is really a Fourier transform of $\overline{Q}$.

Our general wave packet (6 a—6 b) has also in some sense the classical properties of a Kennard packet. The parameters of scale changing $b(\tau)$, $c(\tau)$ (in comparison with the output packet $Q(\zeta', \tau)$, $P(\eta', \tau)$) are simple periodical time functions. These are correlated with the mean square errors in position and momentum, i. e. with the packet width. The quantities $\bar{\xi}, \bar{\eta}$ giving the shift packet $Q'(\bar{\xi}', \tau)$, $\overline{P}(\eta', \tau)$ as compared with the $Q(\zeta', \tau)$, $P(\eta', \tau)$ packet in relation to the centrum of attraction are classical quantities.

3. Let us apply the general formulae (6 a—6 b) to the case where the state, with which $(Q(\zeta', \tau)$ and $P(\eta', \tau)$ are connected, depends upon time only by a phase factor. Only such a property possesses stationary states: $|n'(\tau)\rangle \overset{\text{df}}{=} |n'\rangle e^{-i(n'+1/2)\tau}$. In consequence of (1 a—1 b), we find, according to (6 a—6 b), that if the numbers $\Delta\xi^0_{n'}, \Delta^0_{n'}$ satisfy

$$\Delta\xi^0_{n'} \cdot \Delta\eta^0_{n'} = n' + 1/2, \tag{7}$$

then to the state $|\overline{n}'(\tau)\rangle \overset{\text{df}}{=} e^{-i\tau H} \Omega(\xi_0, \eta_0) \Pi[\Delta\xi^0_{n'}(n'+1/2)^{-1/2}] |n'\rangle$ correspond probability amplitudes given by:

$$\overline{q}_{n'}(\xi', \tau) = \left[\frac{\Delta\xi_{n'}(\tau)}{\sqrt{n'+1/2}}\right]^{-1/2} u_{n'}\left[\{\xi' - \bar{\xi}(\tau)\} \Big/ \frac{\Delta\xi_{n'}(\tau)}{\sqrt{n'+1/2}}\right] \times \tag{8 a}$$

$$\times \exp i \left[\xi' \overline{\eta}(\tau) - \overline{w}(\tau) - (n'+1/2) \operatorname{arctg} \frac{\Delta\eta^0_{n'}}{\Delta\xi^0_{n'}} \operatorname{tg} \tau + \right.$$

$$\left. + \tfrac{1}{2}(\xi' - \bar{\xi}(\tau))^2 \frac{d}{d\tau} \log \Delta\xi_{n'}(\tau) - \xi_0\eta_0/2 + n'\pi/4\right]$$

$$\overline{p}_{n'}(\eta', \tau) = \left[\frac{\Delta\eta_{n'}(\tau)}{\sqrt{n'+1/2}}\right]^{-1/2} u_{n'}\left[\{\eta' - \overline{\eta}(\tau)\} \Big/ \frac{\Delta\eta_{n'}(\tau)}{\sqrt{n'+1/2}}\right] \times \tag{8 b}$$

$$\times \exp i \left[-\eta'\bar{\xi}(\tau) + \overline{w}(\tau) - (n'+1/2) \operatorname{arctg} \frac{\Delta\xi^0_{n'}}{\Delta\eta^0_{n'}} \operatorname{tg} \tau + \right.$$

$$\left. + 1/2(\eta' - \overline{\eta}(\tau))^2 \frac{d}{d\tau} \log \Delta\eta_{n'}(\tau) + \zeta_0\eta_0/2 - n'\pi/4\right]$$

The classical quantities $\bar{\xi}, \overline{\eta}$ can be easily identified with averaged values of ξ and η in the state $\overline{n}'(\tau)\rangle$.

It can easily be proved that the quantities:

$$\Delta\xi_{n'}(\tau) \overset{\text{df}}{=} [\Delta\xi^{02}_{n'} \cos^2\tau + \Delta^{02}_{n'} \sin^2\tau]^{1/2}, \tag{8 c}$$

$$\Delta\eta_{n'}(\tau) \overset{\text{df}}{=} [\Delta\xi^{02}_{n'} \sin^2\tau + \Delta\eta^{02}_{n'} \cos^2\tau]^{1/2} \tag{8 d}$$

are identical with the mean square errors in the discussed state; $\Delta\xi^0_{n)}$, $\Delta\eta^0_{n'}$ are here their initial values. According to (7), only one of them can be chosen arbitrarily. All the quantities in (8 a –8 b) have therefore a clear physical meaning.

We therefore obtained a family of wave packets labelled by parameters: discrete n' and continuous $\xi_0, \eta_0, \Delta\xi^0_{n'}$ which in a natural way generalize those of Kennard (for $n'=0$ our packet (8 a – 8 b) is identical with the Kennard packet).

It can easily be shown that with fixed $\tau, \xi_0, \eta_0, a = \Delta\xi^0_{n'}(n'+1/2)^{-1/2}$ the functions $\{\bar{q}_{n'}\}$ and $\{\bar{p}_{n'}\}$ form complete ortonormal sets in the position and momentum spaces.

The average values of energy in the state $|\bar{n}'(\tau)\rangle$ is given by:

$$\langle H\rangle = 1/2(\xi_0^2+\eta_0^2)+1/2(\Delta\xi^{02}_{n'}+\Delta\eta^{02}_{n'}).$$

It is therefore composed of the classical part, and, let us say, "fluctuating" part.

We introduce now:

$$\delta_n(\varkappa-\bar{\varkappa},\Delta\varkappa)\overset{\mathrm{df}}{=}\left[\frac{\Delta\varkappa}{\sqrt{n+1/2}}\right]^{-1}u_n^2\left[(\varkappa-\bar{\varkappa})\Big/\frac{\Delta\varkappa}{\sqrt{n+1/2}}\right].$$

In view of: $\varkappa\neq\bar{\varkappa}\to\lim_{\Delta\varkappa\to 0}\delta_n(\varkappa-\bar{\varkappa},\Delta\varkappa)=0$ and hence

$$\lim_{\Delta\varkappa\to 0}\int_{-\infty}^{+\infty}d\varkappa f(\varkappa)\delta_n(\varkappa-\bar{\varkappa},\Delta\varkappa)=f(\bar{\varkappa}),$$

we can write:

(9) $$\lim_{\Delta\varkappa\to 0}\delta_n(\varkappa-\bar{\varkappa},\Delta\varkappa)=\delta(\varkappa-\bar{\varkappa}).$$

The probability densities in the position and momentum spaces correlated with $\bar{n}'(\tau)\rangle$ can be written in terms of δ_n, according to (8 a—8 b), as follows:

(10 a) $$\bar{\varrho}_{n'}(\xi',\tau)=\delta_{n'}(\xi'-\bar{\xi}(\tau),\Delta\xi_{n'}(\tau))$$

(10 b) $$\bar{\sigma}_{n'}(\eta',\tau)=\delta_{n'}[\eta'-\bar{\eta}(\tau),\Delta\eta_{n'}(\tau)].$$

This emphasizes the fact that the centres of the discussed packets move in a classical manner. The parameters measuring the packet width depend in a periodical manner on time. If we choose e. g. $\Delta\xi^0_{n'}$ very small, then, according to (7), $\Delta\eta^0_{n'}$ must be very large, so that in view of (8 c), an initially very sharp $\bar{q}_{n'}$ packet acquires a width pulsating between small $\Delta\xi^0_{n'}$, and large $\Delta\eta^0_{n'}$.

If in (10 a—10 b) we return from ξ, η, τ to x, p, t, then we get formulae for probability densities in x and p spaces, from which, in view of (9),

it follows that:

$$\lim_{\hbar\to 0} \bar{\varrho}_{n'}(x', t) = \delta[x' - x_{kl}(t)], \tag{11a}$$

$$\lim_{\hbar\to 0} \bar{\sigma}_{n'}(p', t) = \delta[p' - p_{kl}(t)], \tag{11b}$$

where

$$x_{kl}(t) = x_0 \cos\omega t + p_0 | m\omega \sin\omega t,\ p_{kl}(t) = p_0 \cos\omega t - m\omega x_0 \sin\omega t.$$

The right hand figures in (11a—11b) are independent of n'. It is therefore not true that one definite wave packet corresponds to the classical motion $x_{kl}(t), p_{kl}(t)$.

All our packets (8a—8b) correspond, within the limit $\hbar\to 0$, to classical motion. In all the possible packets $Q(\zeta', \tau)$, $P(\eta', \tau)$ the relation $\lim_{\hbar\to 0} \varrho(x, t) = \delta[x' - x_{kl}(t)]$ applies, however, only to our family of wave packets which is connected with stationary states.

I should like to thank Prof. L. Infeld and Prof. W. Rubinowicz for their kind interest in this work.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

THEORETICAL PHYSICS

The Equation of Motion of the Magnetic Dipole

by

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Communicated by L. INFELD at the meeting of March 15, 1954

We have learned in the physics of elementary particles that the actual sources of the electromagnetic field are electrical charges and magnetic dipoles. The forces acting on an electrical charge have for long been explained by the Lorentz force-law, but the force acting on a magnetic dipole has not yet been studied. The law governing the force acting on the extended magnetic momentum distribution on the one hand (see [1] where further references to this can be found) and the derivation of motion of the point-like magnetic dipole on the other have been studied only during the last few years. Bhabha and Corben [2] and later Mathisson [3] and others have dealt with the motion of the point dipole by means of the relativistic field theory method of Dirac. The investigations, however, did not lead to consistent results, except in the case of a static force acting on a dipole at rest. In the case of a moving dipole, discrepancies were observed in the force exerted by the external (incoming) field, primarily in the terms containing acceleration. The purpose of the present work is to derive the law of motion by the simplest means possible. To attain this, a suitable procedure seems the one which Einstein, Infeld and Hoffmann adapted to the case of the gravitational field. The same procedure was also used successfully by Infeld and Wallace [4] in the electrodynamics for deriving the equation of motion of a point charge. In the present work we shall confine ourselves to the effect of the external field on the magnetic dipole.

The first step in the calculation is to determine the field produced by the dipole. During its motion the magnetic dipole particle of velocity $\mathfrak{v}$ and momentum $\mathfrak{M}$, also exhibits an electrical dipole momentum, the magnitude of which is [5]:

$$\mathfrak{P} = \tfrac{1}{2}\,\mathfrak{v} \times \mathfrak{M}. \tag{1}$$

The density functions of the point-like electrical momentum and magnetic momentum caused by the motion of the former are

$$\mathfrak{p}(\mathfrak{r}, t) = \mathfrak{P}(t)\,\delta(\mathfrak{r} - \mathfrak{r}_0(t)),\quad \mathfrak{m}(\mathfrak{r}, t) = \mathfrak{M}(t)\cdot\delta(\mathfrak{r} - \mathfrak{r}_0(t)). \tag{2}$$

The Maxwell equations determining the field produced by the momentum densities $\mathfrak{g}$ and $\mathfrak{m}$ are

$$\text{(3)} \qquad \operatorname{rot} \mathfrak{H} - \frac{1}{c}\frac{\partial \mathfrak{E}}{\partial t} = \frac{4\pi}{c}\dot{\mathfrak{p}}, \quad \operatorname{div} \mathfrak{E} = -4\pi \operatorname{div} \mathfrak{p},$$

$$-\operatorname{rot} \mathfrak{E} - \frac{1}{c}\frac{\partial \mathfrak{H}}{\partial t} = \frac{4\pi}{c}\dot{\mathfrak{m}}, \quad \operatorname{div} \mathfrak{H} = -4\pi \operatorname{div} \mathfrak{m},$$

the solution of which is obtained by Novobátzky's method [6] in the form

$$\text{(4)} \qquad \mathfrak{E} = \mathfrak{E}^e - \operatorname{grad} \Phi - \frac{1}{c}\dot{\mathfrak{A}} - \operatorname{rot} \mathfrak{a},$$

$$\text{(5)} \qquad \mathfrak{H} = \mathfrak{H}^e - \operatorname{grad} \varphi - \frac{1}{c}\dot{\mathfrak{a}} + \operatorname{rot} \mathfrak{A},$$

where $\mathfrak{E}^e, \mathfrak{H}^e$ mean the external field strengths. The potentials $\Phi, \mathfrak{A}, \varphi, \mathfrak{a}$ satisfy the following equations:

$$\text{(6)} \qquad \Delta \mathfrak{A} - \frac{1}{c^2}\ddot{\mathfrak{A}} = -\frac{4\pi}{c}\dot{\mathfrak{p}} = -\frac{4\pi}{c}\frac{d}{dt}(\mathfrak{P}\delta),$$

$$\text{(7)} \qquad \Delta \Phi - \frac{1}{c^2}\ddot{\Phi} = 4\pi \operatorname{div} \mathfrak{p} = 4\pi \mathfrak{P} \operatorname{grad} \delta,$$

$$\text{(8)} \qquad \operatorname{div} \mathfrak{A} + \frac{1}{c}\dot{\Phi} = 0,$$

$$\text{(9)} \qquad \Delta \mathfrak{a} - \frac{1}{c^2}\ddot{\mathfrak{a}} = -\frac{4\pi}{c}\dot{\mathfrak{m}} = -\frac{4\pi}{c}\frac{d}{dt}(\mathfrak{M}\delta),$$

$$\text{(10)} \qquad \Delta \varphi - \frac{1}{c^2}\ddot{\varphi} = 4\pi \operatorname{div} \mathfrak{m} = 4\pi \mathfrak{M} \operatorname{grad} \delta,$$

$$\text{(11)} \qquad \operatorname{div} \mathfrak{a} + \frac{1}{c}\varphi = 0.$$

For solving these equations we use the approximation method of Einstein, Infeld and Hoffmann. We assume that in our mass system the field quantities can be expanded in a convergent power series according to the (negative) powers of the value c of the velocity of light *in vacuo*. It is evident that the field equations can be satisfied by series involving only even or odd powers:

$$\text{(12)} \qquad \varphi = \sum_{l=0}^{\infty} c^{-2l} \varphi_{2l}, \quad \mathfrak{a} = \sum_{l=0}^{\infty} c^{-2l-1} \underset{2l+1}{\mathfrak{a}}.$$

The subsequent terms of the expansion can be determined on the basis of (9), (10), (11) from the following equations:

$$\text{(13)} \qquad \Delta \varphi_0 = 4\pi \mathfrak{M} \operatorname{grad} \delta, \qquad \Delta \underset{1}{\mathfrak{a}} = -4\pi \frac{d}{dt}(\mathfrak{M}\delta),$$

$$\Delta \underset{2l}{\varphi} = \ddot{\underset{2l-2}{\varphi}}\,, \quad \Delta \underset{2l+1}{\mathfrak{a}} = \ddot{\underset{2l-1}{\mathfrak{a}}}\,, \qquad (l \geq 1) \tag{14}$$

$$\operatorname{div} \underset{2l+1}{\mathfrak{a}} + \dot{\varphi}_{2l} = 0 \qquad (l \geq 0). \tag{15}$$

These equations can be easily solved. With the notation $r = |\mathfrak{r} - \mathfrak{r}_0(t)|$

$$\underset{2l}{\varphi} = -\frac{1}{(2l)!}\frac{d^{2l}}{dt^{2l}}(\mathfrak{M} \operatorname{grad} r^{2l-1}), \quad \underset{2l+1}{\mathfrak{a}} = \frac{1}{(2l)!}\frac{d^{2l+1}}{dt^{2l+1}}(\mathfrak{M} r^{2l-1}). \tag{16}$$

Φ and $\mathfrak{A}$ can be determined in a similar manner. By introducing the above formulas into (4) and (5) the following form of the field strengths is obtained:

$$\begin{aligned}\mathfrak{E} = \mathfrak{E}^e &+ \sum_{l=0}^{\infty} \frac{c^{-2l}}{(2l)!}\frac{d^{2l}}{dt^{2l}}(\mathfrak{P} \operatorname{grad}) \operatorname{grad} r^{2l-1} \\ &- \sum_{l=1}^{\infty} \frac{c^{-2l}}{(2l-2)!}\frac{d^{2l}}{dt^{2l}}(\mathfrak{P} r^{2l-3}) + \sum_{l=0}^{\infty} \frac{c^{-2l-1}}{(2l)!}\frac{d^{2l+1}}{dt^{2l+1}}(\mathfrak{M} \times \operatorname{grad} r^{2l-1}),\end{aligned} \tag{17}$$

$$\begin{aligned}\mathfrak{H} = \mathfrak{H}^e &+ \sum_{l=0}^{\infty} \frac{c^{-2l}}{(2l)!}\frac{d^{2l}}{dt^{2l}}(\mathfrak{M} \operatorname{grad}) \operatorname{grad} r^{2l-1} \\ &- \sum_{l=1}^{\infty} \frac{c^{-2l}}{(2l-2)!}\frac{d^{2l}}{dt^{2l}}(\mathfrak{M} r^{2l-3}) - \sum_{l=0}^{\infty} \frac{c^{-2l-1}}{(2l)!}\frac{d^{2l+1}}{dt^{2l+1}}(\mathfrak{P} \times \operatorname{grad} r^{2l-1}).\end{aligned} \tag{18}$$

Knowing the field strengths, we can use the Einstein-Infeld-Wallace-method to determine the equation of motion [4]. It is well known that the mechanical momentum transmitted from the field to the dipole particle per unit of time can be written with the aid of the Maxwell stress tensor t_{ik} and of the field momentum density $\mathfrak{G}$ in the form

$$\frac{dp_i}{dt} = \int (\partial_k t_{ik} - \dot{G}_i)\, dV. \tag{19}$$

(Repetition of an index implies summation from 1 to 3).

The integration can be extended to a three-dimensional volume containing the dipole in its interior. To avoid the difficulties of the singularity at the dipole, let us introduce the functions ψ_i which are defined by

$$\Delta \psi_i = -\dot{G}_i. \tag{20}$$

By using this, equation (19) can be transformed, according to the theorem of Gauss, into a surface integral:

$$\frac{dp_i}{dt} = \oint (t_{ik} + \partial_k \psi_i)\, df_k. \tag{21}$$

As the divergence of the integrand (the force density) vanishes outside of the dipole, the integrand is independent of the shape of the surface, i. e. it depends only upon the singularity. If we take it that the surface surrounding the dipole is a sphere, the integral is independent of its radius. Thus, in the evaluation of the integral, it suffices to take into account the term depending on r in the form r^{-2} in the integrand.

On the spherical surface surrounding the dipole, i. e. *in vacuo*, t_{ik} is of the form

$$t_{ik} = \frac{1}{4\pi}(E_i E_k + H_i H_k) - \frac{\delta_{ik}}{8\pi}(E_r E_r + H\ H_r). \tag{22}$$

The field momentum density is assumed (apart from quadratic terms in the velocity) to be

$$\mathfrak{G} = \frac{1}{4\pi c}\,\mathfrak{E} \times \mathfrak{H} \tag{23}$$

at every point in the field. By introducing the expressions (17) and (18) into (21), three types of terms are obtained. One of the terms involves the products of the external field components. As the external field has no singularity at the dipole, these terms do not contribute at all to the integral expression (21). There are also terms which contain the products of the components of the external field and of the dipole field. These mixed terms result in the force of the external field acting on the dipole, the calculation of which is our main task. Finally, in the third type of term only the eigenfield of the dipole is involved, i. e. these term do not contain the strengths of the external field. This third type of terms describes the reaction of the field produced by the dipole on its own motion, the determination of which is not dealt with in the present work. The self-force is summarized in a term denoted by K_i.

Thus in the evaluation of (21) we are only interested in the "mixed" terms. The components of the external field are expanded in a Taylor series around the dipole:

$$H_i^e(\mathfrak{r}) = H_i^e(\mathfrak{r}_0) + [\operatorname{grad} H_i^e]_{\mathfrak{r}_0} \cdot (\mathfrak{r} - \mathfrak{r}_0) + \ldots \tag{24}$$

Differentiating with respect to time, the sums representing the eigenfield in (17) and (18), we get a power series in r^{-1}. As we have mentioned above, of these products only the terms of the r^{-2}-th order must be integrated over the spherical surface of radius r surrounding the dipole. If we assume that in our Lorentz frame of reference the dipole is instantaneously at rest ($\mathfrak{v} = 0$), only the terms belonging to the values $l = 0$ and $l = 1$ of the expansion contribute to the integral (21). The substitutions and integrations are tedious but quite elementary and result in the following: the terms resulting from the mixed products in $\oint t_{ik}\, df_k$ are:

$$(25)\qquad \left(\frac{2}{3} M_r \partial_r H_i^e + \frac{1}{3} M_r \partial_i H_r^e\right) + \frac{2}{3c}(\mathfrak{E}^e \times \dot{\mathfrak{M}} + \mathfrak{P} \times \mathfrak{H}^e)_i + \frac{1}{3c^2} H_r^e (M_r \dot{v}_i - M_i \dot{v}_r).$$

The terms resulting from the mixed products in $\oint \partial_k \psi_i \, df_k$ are:

$$(26)\qquad \frac{1}{3c} \frac{d}{dt} (\mathfrak{E}^e \times \mathfrak{M} + \mathfrak{P} \times \mathfrak{H}^e)_i - \frac{1}{3c^2} H_r^e (M_r \dot{v}_i - M_i \dot{v}_r).$$

(It has also been taken into account that $\mathfrak{P}(t) = 0$ according to $\mathfrak{v}(t) = 0$). Considering that the external field satisfies the equation

$$(27)\qquad \text{rot}\, \mathfrak{H}^e - \frac{1}{c} \frac{\partial \mathfrak{E}^e}{\partial t} = 0,$$

the sum of (25) and (26) because of (27) leads to the equation of motion

$$(28)\qquad \frac{\vec{dp}}{dt} = \vec{K} + (\mathfrak{M}\ \text{grad})\, \mathfrak{H}^e + \frac{1}{c} \mathfrak{E}^e \times \dot{\mathfrak{M}} + \frac{1}{c} \dot{\mathfrak{P}} \times \mathfrak{H}^e$$

$$(29)\qquad = \vec{K} + (\mathfrak{M}\ \text{grad})\, \mathfrak{H}^e + \frac{1}{c} \mathfrak{E} \times \dot{\mathfrak{M}} + \frac{1}{c^2} (\dot{\mathfrak{v}} \times \mathfrak{M}) \times \mathfrak{H}^e.$$

The meaning of the last three terms describing the effect of the external field is quite clear. The second term is the translational force acting on the dipole in a non-homogeneous magnetic field. The third is the force acting on the "magnetic current" generated by the variation (acceleration, rotation) of the magnetic momentum in an electrical field. The last is the Lorentz force acting in the magnetic field on the electrical polarisation current, which results from the variation in the electrical dipole momentum of the moving magnet owing to acceleration. Although no experiment till now has shown the existence of a third force term, its existence was nevertheless assumed by Einstein and Laub [7] as early as 1908. (Some authors do not accept it. For a discussion of this question, from the point of view of phenomenological electrodynamics, see [8]).

The method described above is based on quite simple assumptions. The force-law could only be modified if we changed our assumption for the momentum density of the field. The term of the electrical force acting on the magnetic current, which is relevant in the result, could only be modified if the field momentum density expression (23) were completed by a term containing the momentum density $\mathfrak{m}(\mathfrak{r}, t)$, which has a singularity at the dipole. Such a modification, however, would either destroy the symmetry of the four-dimensional energy-momentum-tensor, or, owing to the modification of the Poynting vector, it would lead to sources that produce energy in static fields also.

If the change in the mechanical momentum in an external field is determined, the energy change per unit of time can also be determined. The

result can be obtained by simple calculation on the basis of the formula

$$(30) \qquad \frac{dE}{dt} = -\int \left(\operatorname{div} \mathfrak{S} + \frac{\partial u}{\partial t} \right) dv = -\oint (S_k + \partial_k \psi)\, df_k, \quad \Delta\psi = \frac{\partial u}{\partial t},$$

where u is the electromagnetic energy density and $\mathfrak{S}$ the density of the energy current. In the calculations, however, the form of the expression of u at the dipole plays a decisive role. E. g. the energy density formula

$$u = \frac{1}{8\pi}(\mathfrak{E}\mathfrak{D} + \mathfrak{H}\mathfrak{B}) = \frac{1}{8\pi}(\mathfrak{E}^2 + \mathfrak{H}^2) + \frac{1}{2}(\mathfrak{E}\mathfrak{P} + \mathfrak{H}\mathfrak{M}) \cdot \delta(\mathfrak{r} - \mathfrak{r}_0)$$

leads to a result fundamentally different from the one obtained by the simple

$$u = (\mathfrak{E}^2 + \mathfrak{H}^2)/8\pi.$$

Thus the energy equation is given in the form

$$(31) \qquad \frac{dE}{dt} = W + \dot{\mathfrak{M}}\mathfrak{H} + \dot{\mathfrak{P}}\mathfrak{E} + \int \frac{\partial}{\partial t}\left[\frac{1}{8\pi}(\mathfrak{E}^2 + \mathfrak{H}^2) - u \right] dV,$$

where W is the effect of the self-force.

In conclusion, we note that the force-law (28) agrees for the resting dipole, with the specialized form of the general equation of motion of Mathisson [3], but differs from the result of Bhabha and Corben [2] in the terms containing the acceleration. In our calculation other terms involving acceleration would occur as well, if the (23) formula of the field momentum density were completed by an expression proportional to the velocity of the dipole [1]. (The various theories do not supply consistent information as to whether or not the mechanical momentum $\vec{p}$ of the particle depends on the field quantities).

My thanks are due to Prof. L. Infeld for his help and advice and to the Polish Academy of Sciences for giving me the opportunity — during the course of this work — of being a guest at the Institute of Theoretical Physics of the University of Warsaw.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

EXPERIMENTAL PHYSICS

Scattering of Slow Neutrons by Liquids
Scattering of 80° K-Neutrons in CH_3OH and CH_3I

by

J. A. JANIK

Communicated by H. NIEWODNICZAŃSKI at the meeting of March 15, 1954

In the first part of this work [1] it was suggested that the theory of Sachs and Teller [2], originally conceived in connection with molecular gases, may also be applied to many liquids. The agreement of the experimentally obtained cross-sections with those theoretically evaluated from the theory of Sachs and Teller was then proved on several different liquids (H_2, H_2O, CH_3I). In the same paper was given also a simplified form of the formula of Sachs and Teller for the cross-section for the scattering of slow neutrons by the molecules of a liquid. This simplified formula is

$$\sigma = \sigma_\infty (\mu_1\, \mu_2\, \mu_3\, \mu)^{1/2}, \tag{1}$$

where σ_∞ is the cross-section for zero-energy neutrons of an atom rigidly bound in an infinitely heavy molecule (in the case of hydrogen $\sigma_\infty = 80.10^{-24}\,\text{cm.}^2$), and μ_1, μ_2, μ_3, μ are figures representing the dependence of σ on the ellipsoid of inertia of the investigated molecule.

The theory of Sachs and Teller, applied to gases as well as to liquids, is valid for rigid molecules only. For this reason, in the case of CH_3OH, the cross-section obtained experimentally was considerably smaller than the one theoretically evaluated from formula (1). This effect was interpreted as being due to the influence of the hindered rotation of the proton of the OH-group in the CH_3OH molecule around the CO-axis. As is known from spectroscopical data, this hindered rotation degenerates into torsional oscillation of the wave number $250\,\text{cm}^{-1}$.

A correct theoretical explanation of this effect has been given by Kołos [3]. He obtained the following formula for the cross-section of an atom bound in a molecule performing an internal hindered rotation

$$\sigma_{m_f \varrho_f, m_i \varrho_i} = \overline{b_0^2} \cdot \sigma_{m_f, m_i}, \tag{2}$$

where m denotes the set of the rotational quantum numbers τ, τ', j and ϱ is the quantum number of the hindered rotation. The indices i and f correspond respectively to the initial and final state of the system. $\sigma_{m_f m_i}$ is the cross-section of an atom rigidly bound in a rigid molecule and b_0^2 is a coefficient $\leqslant 1$.

The collisions of 300° K-neutrons with CH_3OH molecules are elastic with respect to the hindered rotation. They are able, however, to cause a great change in the quantum number $\tau (0 \rightarrow 10,\ 2 \rightarrow 11$ etc.). Kołos has calculated that b_0^2 is then about 0.7 for protons of the CH_3-group and about zero for the proton of the OH-group. This theory explains semiquantitatively the small cross-section of the CH_3OH molecule in agreement with the experimental data.

In the present work the measurements of the cross-sections of CH_3I and CH_3OH molecules for 300° K-neutrons were repeated and measurements for 80° K-neutrons were also made. The following effects were expected:

1. It follows from formula (1) that the cross-section for the scattering of slow neutrons by the molecules of a liquid is independent of the energy of the neutrons (within some limits of this energy). Therefore there should be no energy dependence in the cross-section of CH_3I molecules.

2. The 80° K-neutrons may cause only a slight change in the quantum number τ. It follows from the theory of Kołos that the coefficient b_0^2 would then not differ considerably from 1 and the diminution in the value of the cross-section of the CH_3OH molecule for 80° K-neutrons with respect to the value obtained from formula (1) would be smaller.

The apparatus consisted of a source of photoneutrons (200 mg. Ra surrounded by beryllium powder), slowed down by a 6 cm. layer of paraffin wax, and a boron-lined, ionisation chamber as a detector of thermal neutrons. 80° K-neutrons were obtained in an arrangement similar to that described by Westcott and Niewodniczański [4].

The results are given in Table I.

TABLE I

Substance	Cross-section per molecule for 300° K -neutrons obtained in previous experiments [1]	Cross-section per molecule for 300° K -neutrons obtained experimentally in the present work	Cross-section per molecule for 80° K -neutrons obtained experimentally in the present work	Cross-section per molecule evaluated from formula (1)
CH_3I	$(195 \pm 10) \cdot 10^{-24}$ cm.²	$(204 \pm 10) \cdot 10^{-24}$ cm.²	$(193 \pm 12) \cdot 10^{-24}$ cm.²	$195 \cdot 10^{-24}$ cm.²
CH_3OH	$(180 \pm 7) \cdot 10^{-24}$ cm.²	$(180 \pm 6) \cdot 10^{-24}$ cm.²	$(227 \pm 10) \cdot 10^{-24}$ cm.²	$247 \cdot 10^{-24}$ cm.²

It can be seen from Table I that the results in the case of CH_3OH and CH_3I, using 300° K-neutrons, are in agreement with those obtained in part I of this work.

There is a rather good agreement between the cross-sections calculated from the theory of Sachs and Teller and those experimentally obtained for CH_3I molecules for 300° K and 80° K-neutrons. Within the limits of experimental errors there is no dependence on the energy of neutrons.

In the case of CH_3OH the result for 80° K-neutrons supports the theory of Kołos. The 80° K-neutrons have an energy about 3 times lower than that of the 300° K-ones and therefore cause much fewer changes of $\tau(0 \to 4,\ 1 \to 4$ etc). For these changes of τ the coefficient b_0^2 is about 0.95 for protons of the CH_3-group and about 0.4 for the proton of the OH-group. Therefore, according to Kołos' theory, the cross-section of a CH_3OH molecule for 80° K-neutrons will have a value lying between that obtained by using 300° K-neutrons and the one calculated from formula (1).

I wish to express my gratitude to Prof. H. Niewodniczański for his kind interest in this work.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

CHEMISTRY

Hittorf's Effect in a Binary Electrolyte Solution from the Point of View of the Thermodynamics of Irreversible Processes

by

B. BARANOWSKI

Communicated by M. ŚMIAŁOWSKI at the meeting of December 14, 1953

Introduction. Diffusion in an isothermal electrolytic solution is usually associated with the appearance of an electric field which accelerates the less mobile ion and restrains the faster one. This diffusion potential was theoretically determined by means of classical methods [1] and by thermodynamics of irreversible processes, based on Onsager relations [2]. According to these relations, the diffusion potential should be considered as a "cross-effect" of the gradients of concentration and of the electric potential. Onsager relations require the possible existence of a reverse phenomenon, i. e. the appearence of a concentration gradient in presence of an external electric field. This reverse "cross-effect" is known in the electrolytical process as Hittorf's effect. The condition for the stationary state of this effect is given below.

Assumptions. One has to consider an isothermal dilute solution of a binary strong electrolyte, located between parallel electrodes, connected with a source of direct current. The considerations given below apply only to such sections of the electrolyte in which the electrode processes do not themselves play any role. The convection currents and possible space charge are neglected. The activity coefficients of both ions are regarded as being equal to unity, and the stationary state is assumed to be a state in which the anions and the cations take an equal share in the transport of the electric charges.

Phenomenological relations and fluxes. According to general thermodynamic assumptions of irreversible processes, equations describing the fluxes J_l may be written as follows:

$$J_l = \sum_{l=1}^{n} L_{lk} X_k. \tag{1}$$

In this equation n equals the number of fluxes, L_{ik} the phenomenological coefficients and X_k the thermodynamic forces.

In addition the coefficients L_{ik} fulfill the Onsager relations

$$L_{ik} = L_{ki} \qquad i, k = 1, 2, \ldots, n. \tag{2}$$

In this case we have to do with four fluxes, that of the ions J_1 and J_2, of the solvent J_3 and of the electric current density J_4 respectively. The values J_1, J_2 and J_3 indicate the number of moles in each of the given components being transferred per unit of time through the unit cross-section. Because of dilution of the solution, the value J_3 may be neglected. The electric density of the current is associated with the values J_1 and J_2 by the equation:

$$J_4 = e_1 J_1 + e_2 J_2,$$

in which e_1 and e_2 are the molar ionic charges. Therefore only two J-values are independent. Equations (1) describe the diffusion process and the ion migration in an external electric field and also the above mentioned "cross effects".

Thermodynamical forces. In the system under consideration two thermodynamical forces, X_1 and X_2, appear in both ions. They are expressed as follows [3]:

$$\begin{aligned} X_1 &= -\operatorname{grad}\mu_1 - e_1 \operatorname{grad}\varphi, \\ X_2 &= -\operatorname{grad}\mu_2 - e_2 \operatorname{grad}\varphi, \end{aligned} \tag{3}$$

where $\mu_1 \mu_2$ are the chemical potentials of the ions, φ — the electric potential. Because we are concerned here with an ideal solution of a binary electrolyte in an external electric field, we can write:

$$X_1 = -\frac{RT}{c}\frac{dc}{dx} - e_1 \frac{\Delta\varphi_0}{\Re}\varrho; \quad X_2 = -\frac{RT}{c}\frac{dc}{dx} + e_1 \frac{\Delta\varphi_0}{\Re}\cdot\varrho, \tag{4}$$

where R is the gas constant, T — the absolute temperature, c — concentration, $\Delta\varphi_0$ — the potential difference applied to the examined section of the solution, ϱ — the specific resistance, x — the coordinate, $\Re$ — the total resistance.

Phenomenological coefficients. According to equations (1) and (2), in the problem being considered, we have three independent phenomenological coefficients. They can be determined by applying equations (1) to the following particular cases:

1. In the absence of an external electromotive force ($\Delta\varphi_0 = 0$) equations (1) describe the diffusion process of both ions. The stationary state is given by: $J_1 = J_2$. Equations (1) are then expressed by an equation representing Fick's law: $J_1 + J_2 2 = -D dc/dx$, where D is the diffusion coefficient. The electric terms of equations (4) have been replaced by Henderson's equations [3].

2. In the case of absence of the concentration gradient in the solution, and in the presence of an external electromotive force, equations (1) are reduced to the Ohm law: $e_1 J_1 + e_2 J_2 = \Delta\varphi_0/\Re$.

Except for the particular cases mentioned above we apply the definition of the transport number:

$$t_1 = \frac{J_1}{J_1 - J_2}.$$

The three conditions mentioned above determine the independent phenomenological coefficients:

$$L_{11} = \frac{Dc}{2RT} + \frac{t_1^2}{\varrho e_1^2},$$

$$L_{12} = \frac{Dc}{2RT} - \frac{t_1 \cdot t_2}{\varrho e_1^2}, \tag{5}$$

$$L_{22} = \frac{Dc}{2RT} + \frac{t_1^2}{\varrho e_1^2},$$

where ϱ equals the specific resistance.

These last equations obviously fulfill the conditions of the extended second principle of thermodynamics:

$$L_{11} \geqslant 0; \quad L_{22} \geqslant 0; \quad L_{11} L_{22} - L_{12} L_{21} \geqslant 0.$$

The stationary state. In accordance with the definition mentioned in the introduction, the condition for a stationary state is given by the equation:

$$J_1 = -J_2. \tag{6}$$

Hence, by adding correspondingly the left and the right parts of equations (1) we obtain:

$$(L_{11} + L_{21}) X_1 + (L_{12} + L_{22}) X_2 = 0. \tag{7}$$

Introducing into the last equation the expressions for the phenomenological coefficients (5) and using the Onsager relation (2), we get an equation expressing the concentration gradient in the stationary state (6):

$$\frac{dc}{dx} = -\frac{\dfrac{\Delta\varphi_0 \cdot (t_1 - t_2)}{\Re \cdot e_1}}{2D + \dfrac{RT}{c} \cdot \dfrac{(t_1 - t_2)^2}{\varrho \cdot e_1^2}}. \tag{8}$$

Discussion. Equation (8) indicates that the concentration gradient appears only if the transport numbers of the opposite charged ions are different. Because this condition must also be fulfilled in order to ensure the appearance of a diffusion potential, the Hittorf's effect is, therefore, inseparably connected with the existence of a diffusion potential in the same electrolytic solution.

Equation (8) shows that the concentration gradient in the stationary state of the Hittorf effect diminishes as the diffusion coefficient increases. The physical meaning of this conclusion is self evident.

The stationary state defined above (6) denotes simply the equality of the effective transport numbers of the opposite charged ions. The concentration gradient is therefore directed in such a way that the diffusion accelerates the motion of the less mobile ion, while retarding that of the more mobile one.

In contrast to the deduction of the diffusion potential, it was not possible in this case to avoid the necessity of expressing the separate phenomenological coefficients. In the case of a stationary state defined by the equation $J_1 = J_2$ it is easy to prove that one of the conditions taken under consideration is sufficient to determine the phenomenological coefficients.

In equations (4), the term respecting the possible diffusion potential was not introduced. This omission seems to be physically justified, because, whatever its direction, it does not exert any influence on the equalization of the velocities of the oppositely charged ions, since they are moving in an external electric field in opposite directions.

I take this opportunity of expressing my thanks to Prof. K. Gumiński for his interest and kind assistance.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

CHEMISTRY

The Pre and Post-critical Regions of One-Component Systems. Pressure and Compressibility Changes on the McIntosh Isochore

by

A. KRĘGLEWSKI

Presented by W. ŚWIĘTOSŁAWSKI on January 5, 1954

1. Introductory remarks

A relatively large number of papers have been published dealing with deviations from the continuity theory in the pre-critical region of liquids. A convincing proof of lack of continuity is provided by the McIntosh and Maass isochore [2], which shows the differences in the state of systems heated or cooled at constant volume and at temperatures lying on both sides close to that of the disappearence of the meniscus T_m (Fig. 2-A). The above mentioned authors have suggested distinguishing the following states:

1) State A is a system heated from lower temperatures to T_m. In this case, the two-phase system, in spite of being heated to higher temperatures than T_m. remains until T_d is reached, at which point the system becomes homogeneous.

2) State B is a system cooled down from T_d. It remains homogeneous until the temperature coincident with the appearence of the meniscus $T_r \leqslant T_m$ is reached.

3) State C is a system obtained by cooling below T_r from state B. The difference in the densities of the phases is smaller in state C than it is in state A.

The measurements of pressure [3] do not offer any conclusive answer as to the relative stability of each of these states. Apparently above T_m the pressure established in state A is smaller than that in state B. Taking into consideration the effect of compression by "temperature gradient", we may conclude [4] that the differences in the phase densities and pressures of A and C below T_m are due only to differences in the amount of dispersed vapour in the liquid phase and, vice versa, of dispersed liquid particles in the vapour phase.

The true cause of the hysteresis of density above T_m is not known.

2. Experimental part

Fig. 1 represents an apparatus for taking comparative measurements of very small changes in pressure and compressibility of the system. The apparatus consists of a *U*-tube, of which the two arms, separated by mercury, have been filled with the same liquid, namely propylene. A description of the purification of propylene and other technical details will be published elsewhere [1]. The average density of the propylene in each section of the *U*-tube was somewhat lower than the critical one: in the left arm it equalled 0.213, in the right one — 0.218 g./ccm. The *U*-tube was placed in a pipe, 4.5 cm. in diameter, and a constant temperature was maintained by means of a stream of water from a Höppler ultrathermostat.

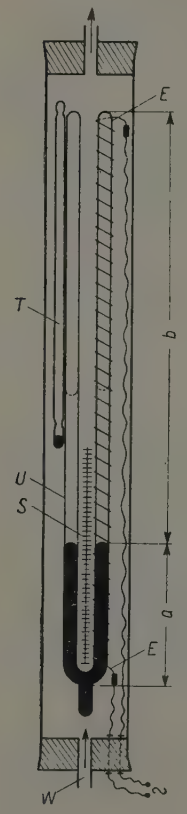

Fig. 1. Apparatus for measuring small pressure changes and compressibility differences in the pre-critical region of liquids. *E* is a resistance wire; *U* a thick walled *U*-tube; *T* a short standard thermometer; *W* a thermostat liquid inlet

As long as the compressibility coefficient β in both systems is infinite, the difference Δp between the two mercury levels is practically nil (apart from the difference between the hydrostatic pressures of the two systems). At the moment when β reaches a finite value, the mercury level in the right arm becomes lower than that in the left one. This produces some changes in the densities of both systems, which can be neglected if the length b of the part of the arm filled with fluid is great in comparison to the Δp. Here $b = 21.3$ cm., $a = 7.2$ cm. (Fig. 1).

In the next stage of the experiment the right arm was heated by means of a short heat impulse. A resistance wire *E*, wound round the tube and isolated by a thin layer of nylon, was used. The left arm was kept at a constant temperature $T \geqslant T_m$. When the difference in the mercury levels reached the maximal value 140 mm. (i. e. when the temperature in the right arm was somewhat higher) the current was discontinued, and the temperature in both arms again became equal. The values of Δp were then determined. These "heat impulses" were repeated until a constant value was obtained for Δp, after equalization of the temperatures in both arms had been established.

Two series of measurements (1 and 2, Fig. 2-B) of this kind were taken, in order to find out whether the results obtained in series 1 were

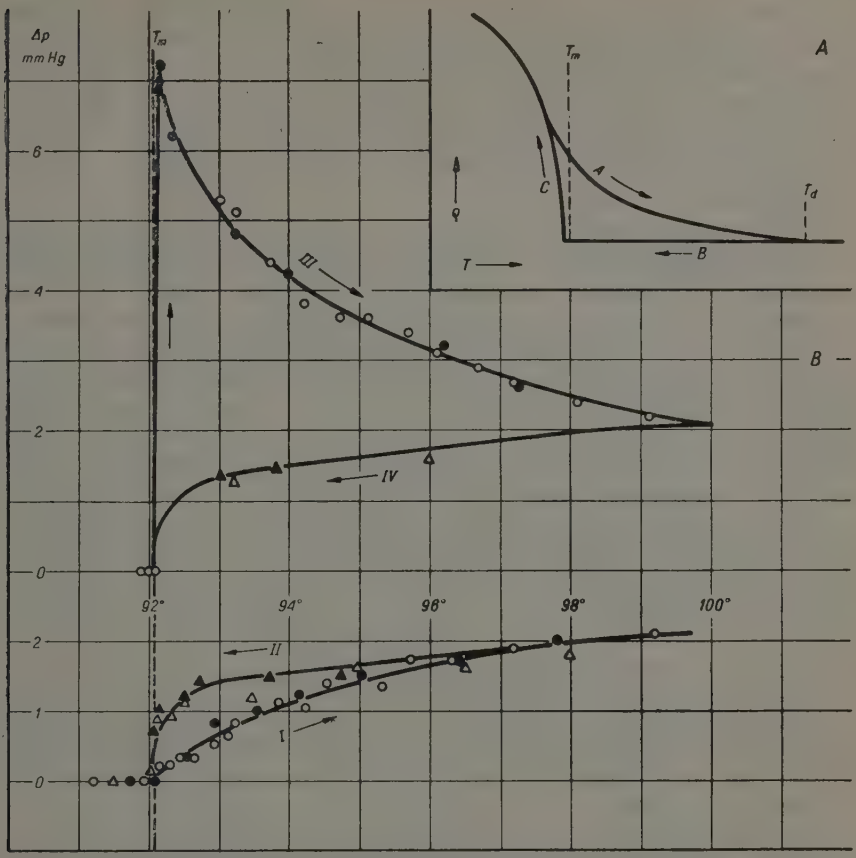

Fig. 2-A. The McIntosh isochore. The density differences ϱ of the gaseous and condensed phase are plotted against temperature

Fig. 2-B. Pressure and compressibility changes in the pre-critical region of propylene. $T_m = T_r = 92.05°$ C. Curve I — heating without heat impulses. Curve II — cooling from 100° without heat impulses. Curve III — heating with heat impulses. Curve IV – cooling from 100° with heat impulses

○△ — series 1, ●▲ — series 2

reproducible when the contents of the tube were mixed and the previous density difference of the systems was, as far as possible, re-established (ser. 2).

3. Results and discussion

a. Heating and cooling without heat impulses (temperature in both arms permanently equal).

Curve I (Fig. 2-B) shows that just above $T_m = T_r = 92.05^0$ C. compressibility β becomes finite. State A is established in both arms. In a system cooled down from 100° (curve II, state B) at a given temperature β is smaller (Δp greater) than in state A. According to Murray and Mason [5], the so-called gravitational effect is proportional to β. It follows that the hysteresis of density on the McIntosh isochore is caused primarily by changes in β.

b. Heating and cooling with the introduction of heat impulses.

After each heat impulse the contents of the left arm of the tube were submitted to isothermal compression which increases the stability of the clusters. The contents of the right arm expanded, because the temperature of the latter rose for a moment to a value considerably higher than T_d. This produced a practically complete splitting of clusters (as described by Maass and Geddes [3]). Thus, after each of the heat impulses, state A was established as before, in the left arm, and state B, in the right one. The difference observed between curves III and I is associated with the difference in pressure in states B and A at a given temperature and "constant" volume (just above T_m, $\Delta p = \sim 0.01$ atm.). It is self evident that on cooling down the systems, starting from 100° or from some higher temperature, the heat impulses do not exert any influence on the values of Δp: curve IV is identical with curve II (both corresponding to state B in each arm).

It is well known that vapour pressure increases with the curvature of the phase boundary. Therefore the increase in pressure in state B is caused by a decrease in the size of the clusters: they are now too small to undergo sedimentation. This is a second reason for the existence of hysteresis of density.

The passage from A to B is accompanied by an increase in entropy [6]. Consequently, clusters in state B are less ordered than in state A.

Below temperature T_m only one state of stable equilibrium is possible.

I wish to express my thanks to Prof. W. Świętosławski for his help and assistance.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

CHEMISTRY

Blocking of the Sorption Capacity of a Sorbent-Kationite

by

M. KRZYSZTOFOWICZ and W. WÓYCICKI

Presented by W. ŚWIĘTOSŁAWSKI on January 18, 1954

1. Blocking effect on Ion-Exchange Capacity. In 1950 it was suggested by W. Świętosławski [1] that the terms "sorbent-ionites" and "ionite-sorbents" should be applied to ion exchangers with a more pronounced sorption or ion exchange capacity. A typical sorbent-kationite is sulfonated coal, "Escarbo", manufactured in Poland. This product was chosen for experiments aimed at blocking the sorption capacity by an adequately chosen substance. In this paper we describe experiments, in which pyridine served as the blocking substance.

It seemed to be important to answer the following two questions: first, whether or not the ion exchange capacity underwent a change after the sorbent-kationite had been blocked by pyridine; secondly, whether the blocking could prevent the further sorption or replacement of pyridine by isomeric nicotinic acids.

In this paper, experiments relating to the first question are briefly described. More details will be published elsewhere [2].

2. Blocking of "Escarbo" with Pyridine. After the "Escarbo" sample had been treated with acid and washed, the blocking was carried out at 20° C. (E_{20}) or at 80° C. (E_{80}) either in an aqueous solution of pyridine or in its vapour.

Two samples were used, one dried at 20° C.; the other at 80° C. The ion exchange characteristics were made by a solution of potassium chloride, and the following data, expressed in K^+ equivalent values, were obtained: E_{20} — 0.638 mval./g. and E_{80} — 0.521 mval./g. of "Escarbo".

The experiments showed that 0.273 g. of pyridine was sorbed by one gram of the sample from its aqueous solutions. In the case of blocking by vapour phase the following values for the sorption of pyridine were found: E_{20} — 0.207 g./g. and E_{80} — 0.306 g./g.

3. Amounts of Sorbed Pyridine Washed out from Blocked "Escarbo". In Table I are given the amounts of pyridine washed out by water.

TABLE I

Amounts of pyridine washed out from 1 g. of blocked "Escarbo"

Type	Blocking by 20% pyridine solution	Blocking by pyridine vapours at 20° C.	Blocking by pyridine vapours at 80° C.
E_{20}	0.191	0.157	0.138
E'_{20}	0.223	0.184	0.161
E_{80}	—	0.152	0.104

E'_{20} is calculated per one gram of dehydrated sample.

From the data given in Table I it can be seen that the smallest amounts of pyridine removed by washing were found for the samples which had been treated with pyridine vapours at 80° C.

4. Removal of Sorbed Pyridine by Heating at 80° C. A series of experiments were carried out with the purpose of removing the sorbed pyridine from "Escarbo" by heating for two days at 80° C. Table II contains the data obtained.

TABLE II

Amounts of pyridine removed from "Escarbo" by heating at 80° C.

Type	Blocking by 20% pyridine solution	Blocking by pyridine vapours at 20° C.	Blocking by pyridine vapours at 80° C.
E_{20}	0.178	0.091	0,018
E'_{20}	0.208	0.106	0.021
E_{80}	—	0.170	0.170

The highest resistance against heating was observed in the case of "Escarbo", dried at 20° C., and then submitted to the action of pyridine vapours at 80° C.

5. Change in the Ion-Exchange Capacity of Blocked "Escarbo". A static method for determining the ion exchange capacity was used. Hydrogen ions were replaced by potassium ones by the action with aqueous potassium chloride solution. Known amounts of that solution were added to a known amount of "Escarbo" blocked by pyridine. As a result of ion exchange, a solution of hydrochloric acid was formed. Some of the latter could react with the desorbed pyridine. The amount of this side-reaction was checked by evaporating the solution of potassium chloride which remained and by heating the salt up to 240° C., in order to remove not only the free hydrochloric acid but also that which had formed pyridine hydrochloride. In Table III the result of the ion exchange is given.

TABLE III

Working ion exchange capacity of samples of "Escarbo" blocked by pyridine

Type	Blocked by 20% pyridine solution	Blocked by pyridine vapour at 20° C.	Blocked by pyridine vapour at 80° C.
E_{20}	0.544	0.540	0.577
E'_{20}	0.655	0.630	0.672
E_{80}	—	0.614	0.582

The results obtained show that blocking of the sorption capacity of "Escarbo" produces relatively small changes in its working ion exchange capacity. In some cases, instead of a decrease, even an increase of that capacity was noticed.

Summary

1. Experiments aimed at blocking the sorption capacity of a typical sorbent-ionit were carried out. A sulfonated coal was blocked by pyridine.

2. The properties of a blocked kationite depend on the physical conditions under which the blocking is carried out.

3. There was an insignificant change in the exchange capacity of the blocked kationite "Escarbo" as compared with the unblocked one.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

CHEMISTRY

Sorption of a Mixture of Isometric Nicotinic Acids by an Ionite after Blocking its Sorption Capacity by Homologues of Pyridine

by

M. KRZYSZTOFOWICZ and W. WÓYCICKI

Presented by W. ŚWIĘTOSŁAWSKI on January 18, 1954

The first paper of this series dealt with the ion exchanger "Escarbo", which is characterized by a large sorption capacity, both before and after it has been blocked by pyridine.

In the experiments described in this paper we used the same sample of H^+ kationite (sulfonated coal, called "Escarbo", produced in Poland), the sorption capacity of which had been blocked by pyridine or other pyridine bases. Our purpose was to ascertain how much of the isomeric nicotinic acids could be sorbed by each of the samples. For this purpose, "Escarbo", in its H^+ form, was submitted to the action of aqueous solutions of different pyridine bases at 20° C. A mixture of isomeric nicotinic acids, close to the composition corresponding to their eutectic composition, was used. An aqueous solution of this mixture, containing 1 g. of the two acids in 100 ml. of water, was used.

The following pyridine bases were used for blocking the sorption capacity of "Escarbo": 2-picoline, 2,6-lutidine and 2,4,6-collidine. After the samples of "Escarbo" had been blocked, each by a different base, they were each brought in contact for 15 minutes with the nicotinic acid solution. The latter was stirred, filtered and then analysed. The samples were then dried for 75 hours at 90° C.

More details concerning the method of the analysis will be given in the Polish journal "Roczniki Chemii".

Table I contains the results thus obtained. Coefficient w, which is equal to the relation between the amounts of the substance sorbed by the blocked and unblocked "Escarbo" respectively, is given in the last column. It is obvious that $w = 0$, if the blocked sorbent is not able to sorb any of the acids. On the other hand, if $w = 1$, this means that the blocked sample sorbs the same quantity of the nicotinic acids as the unblocked one.

TABLE I

Nicotinic acids sorbed by "Escarbo" blocked by homologues of pyridine

Base used for blocking	ml. of nicotinic acid solution per g. blocked sample	Per cent of nicotinic acids sorbed	w
unblocked sample	10 ml.	71%	—
pyridine		20%	0.28
2-picoline		11%	0.14
2,6-lutidine		8%	0.11
2,4,6-collidine		4%	0.06

The respective amounts of pyridine bases removed from the "Escarbo" samples by desorption (chromatographic exchange) were too small to be determined.

Summary

1. In the series of pyridine bases: 2-picoline, 2,6-lutidine, 2,4,6-collidine the last is the most effective for blocking the sorption capacity of "Escarbo" sulfonated coal.

2. The term blocking capacity w has been used to characterize the ratio between the amount of substance sorbed by 1 g. of a blocked ion exchanger and the amount sorbed by 1 g. of an unblocked one. In the case considered in this paper the blocking capacity of the different pyridine bases are given in the last column of Table I.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

Application of a Blocked Kationite for Separating the Nicotinic Acids from Potassium Ions

by

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Presented by W. ŚWIĘTOSŁAWSKI on January 18, 1954

1. Introductory Remarks. Basing our work on the observations described in two previous papers we tried to separate mixtures of nicotinic acids from aqueous solutions by removing potassium ions by means of an ion exchange column filled with the kationite called "Escarbo" which is manufactured in Poland. Before use, several samples of the latter were each blocked separately by different pyridine bases. It should be emphasized that the experiments showed that, without blocking the sorption capacity of the ionite, the potassium ion exchange was always associated with a considerable sorption of nicotinic acids, so that no proper separation could be achieved.

2. Effect of Blocking by Different Pyridine Bases. In each of five small glass columns of equal size (7 mm. in diameter and 300 mm. in length) were placed five grams of the respective H^+ "Escarbo" samples. All, except one, of the latter were blocked, one by pyridine and the three others by the bases: 2-picoline, 2,6-lutidine and 2,4,6-collidine respectively. 20% solutions of the respective bases were used for blocking and the operation was carried out as previously described. Five 59 ml. quantities of the solutions which contained 0.258 g. potassium chloride and 0.5 g. of a mixture of nicotinic isomeric acids were slowly passed through the columns containing the blocked and unblocked samples of "Escarbo".

The mixture of isomeric nicotinic acids differed slightly from the eutectic composition formed by these acids. In fact it was the mother liquor obtained by Bylicki and Lisicki [1] in the course of their investigations into the separation of the constituents of this eutectic. After the solutions mentioned above had been passed through their respective columns, the contents of each column were washed with water. The solutions thus obtained by washing were added to the corresponding effluents, and afterwards analyzed. The results of these experiments are presented in Table I.

TABLE I

Exchange capacity and amount of isomeric nicotinic acids sorbed by "Escarbo" blocked by different pyridine bases

	Unblocked "Escarbo"	Blocked by			
		pyridine	2-picoline	2,6-lutidine	2,4,6-collidine
Working ion exchange capacity	0.33	0.29	0.29	0.29	0.29
g. of nicotinic acids sorbed by 100 g. of "Escarbo"	7.0—8.0	1.1—1.5	1.0	0.6	0.2

The results of these experiments show that the presence of nicotinic acids in the solution of potassium chloride exerts a very considerable influence on the ion exchange working capacity, reducing it to about 50 per cent of its original value. It should be emphasized that the process is complicated by side-reaction because the blocked ion exchanger is of an amphoteric character, serving at the same time both as anionite and kationite. Some side-reactions associated with the change in the *pH* value established in the column could also take place. Further experiments will throw some light on their nature.

Summary

1. The ion exchange working capacity and the sorption of isomeric nicotinic acids on a kation exchanger, of which the sorption capacity had been blocked by different pyridine bases, were examined.

2. It was found that the sorption of isomeric nicotinic acids decreased when compared with the sorption on unblocked (7.0—8.0), and on blocked ion exchanger with pyridine (1.1—1.5), 2-picoline (1.0), 2,6-lutidine (0.6) and 2,4,6-collidine (0.2).

3. The presence of isomeric nicotinic acid in the solution of potassium chloride produced a 50% decrease in the kation exchange working capacity of "Escarbo" — a product obtained by sulfonation of coal.

We wish to express our thanks to Prof. W. Świętosławski for his valuable suggestions during the course of these three investigations.

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

CHEMISTRY

X-Ray Analysis and Magnetic Susceptibilities of Tantalum Hydrides

by

B. STALIŃSKI

Presented by W. TRZEBIATOWSKI on February 11, 1954

A series of 15 tantalum hydrides was prepared under carefully maintained vacuum conditions. Pure degassed tantalum powder and known volumes of hydrogen produced through thermal decomposition of titanium hydride were used [1]. Spectroscopic examination of tantalum metal showed traces (10^{-3} %) of iron and nickel. Hydrogen absorption was carried out at 300°; samples when rapidly cooled attained compositions up to $TaH_{0.52}$, samples with a greater hydrogen content, up to $TaH_{0.75}$, were prepared at lower temperatures ($< 300°$).

The results of X-ray analysis by powder methods (normal and Preston cameras) are presented in Table I and Fig. 1. A solubility of 27 at % hydrogen, i. e. $TaH_{0.37}$, occurs in the α-tantalum phase, much more than was found by G. Hägg ($TaH_{0.14}$) [2]. The lattice constant of tantalum expands gradually from 3.306 to 3.363 Å. A narrow heterogeneous range ($\alpha + \beta$) follows, extending between $TaH_{0.37}$ and $TaH_{0.47}$. The β-phase represents a rhombic distorted tantalum lattice. The distortion increases continuously with the hydrogen content, a fact which is clearly evident with non-orthogonal coordinates ($a = b \neq c$, $\gamma \neq 90°$). The β-phase is identical with the γ-phase of G. Hägg, but in no case was the hexagonal phase found, noted by this author (β). Probably it represents a tantalum nitride. This view is also supported by other authors [3], whose work was published after these experiments were finished. Their results differ quantitatively from the results presented here.

The magnetic susceptibilities of tantalum hydrides were not known. They were determined by means of the Gouy method in a temperature ranging from 80 to 290° K and were practically independent of the field intensity. The results obtained for 11 samples are shown in Table I and Fig. 2. The susceptibility of tantalum metal (χ_g 290° K $= 0.844 \pm 0.005 \cdot 10^{-6}$) is in close agreement with the susceptibility determined at 293° K ($\chi_g = 0.8490 \cdot 10^{-6}$) for spectroscopic standardised metal [4] and differs only slightly from the

value χ_g 298° K = $0.827 \cdot 10^{-6}$ given by other authors [5]. The temperature coefficient is small but negative.

TABLE I

Lattice constants and magnetic susceptibilities of tantalum hydrides

	Lattice constants Å			Magnetic susceptibilities	
	α-phase	β-phase		80° K $\chi_g \cdot 10^6$	290° K
	a	b	c		
1. Ta	3.306			0.864	0.844
2. $TaH_{0.04}$	3.314			0.844	0.829
3. $TaH_{0.14}$	3.325			0.800	0.795
4. $TaH_{0.22}$	3.338			0.780	0.774
5. $TaH_{0.265}$	3.349				
6. $TaH_{0.325}$	3.353			0.736	0.730
7. $TaH_{0.385}$	3.361	3.361	3.391		
8. $TaH_{0.405}$	3.365	3.365	3.392	0.700	0.691
9. $TaH_{0.435}$	3.366	3.366	3.392		
10. $TaH_{0.455}$	3.364	3.364	3.391	0.689	0.678
11. $TaH_{0.47}$	3.363	3.363	3.391	γ	
12. $TaH_{0.52}$		3.370	3.402	89.72° 0.665	0.647
13. $TaH_{0.635}$		3.383	3.424	89.58° 0.571	0.555
14. $TaH_{0.705}$		3.392	3.439	89.52° 0.510	0.505
15. $TaH_{0.735}$		3.394	3.441	89.52° 0.453	0.457
16. $TaH_{0.75}$		3.396	3.448	89.50° 0.420	0.424

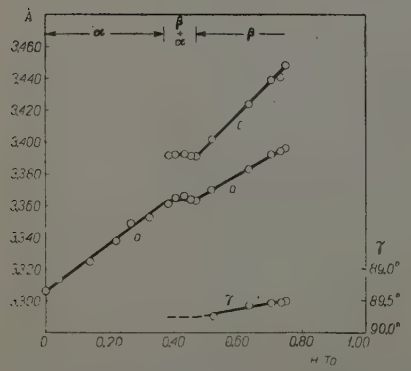

Fig. 1. Lattice constants of tantalum hydrides

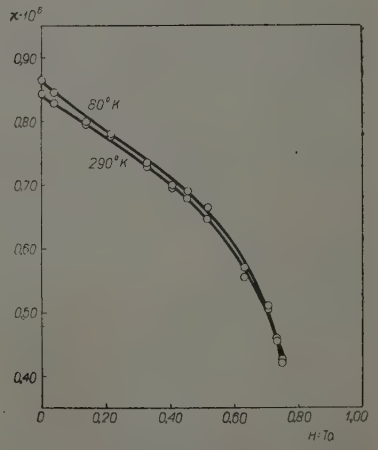

Fig. 2. Magnetic susceptibilities of tantalum hydrides

With increasing hydrogen content the magnetic susceptibility of tantalum diminishes considerably, attaining the value $\chi\ 290^0\,K = 0.424 \cdot 10^{-6}$ at $TaH_{0.75}$. Extrapolation for higher hydrogen content would probably result, between $TaH_{0.8}$ and $TaH_{0.9}$, in susceptibility being zero, as it occurs in the palladium hydrogen system at $PdH_{0.64}$ [6]. The small negative temperature coefficient of tantalum rises with the hydrogen content and appears to be practically zero at higher hydrogen content. In general the magnetic properties of tantalum hydrides correspond closely to the niobium-hydrogen system [7].

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BULLETIN DE L'ACADÉMIE
POLONAISE DES SCIENCES
Cl. III — Vol. II, No. 5, 1954

CHEMISTRY

The Behaviour and Constitution of Active Re (IV)-Complexes

by

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Communicated by W. TRZEBIATOWSKI at the meeting of February 22, 1954

In previous investigations it was established that the reduction of $KReO_4$ in concentrated HCl solutions leads to the formation of two new complex compounds $K_2[ReOHCl_5]$ and $K_4[Re_2OCl_{10}]$ which remain in mutual equilibrium [1], [2]. These compounds are chemically active, in contrast to $K_2[ReCl_6]$ which remains stable even in the presence of such oxidation agents as $KMnO_4$, H_2O_2 and others. In order to explain the constitution of these active compounds, the optical properties and electrical conductivities of their solutions were studied and magnetic measurements were taken of the solid salts.

The active complexes of Re(IV) were obtained by reduction of 0.5 M $KReO_4$ solutions in concentrated HCl with HJ and fractional crystallisation. The methods used have already been described in previous publications [1], [2]. ($K_4[Re_2OCl_{10}]$ — found: Re — 41.2%, Cl — 39.3%, K — 17.3%, O — 2.2%, calc.: Re — 41.6%, Cl — 39.4%, K — 17.4%, O — 1.8%; $K_2[ReOHCl_5]$ — found: Re — 40.6%, Cl — 38.7%, K — 17.1%, OH — 3.6%, calc.: Re — 40.6%, Cl. — 38.6%, K — 17.1%, OH — 3.7%).

$K_4[Re_2OCl_{10}]$ was also prepared directly by slow reduction at temperatures lower than 10° C, of solutions containing an excess of solid $KReO_4$. This process lasted for three weeks. The substance was then crystallized at a temperature of 10° C. under vacuum [3]. (Found: Re — 41.3%, Cl — 39.7%, K — 17.5%, O — 1.5%, calc.: Re — 41.6%, Cl — 39.4%, K — 17.4%, O — 1.8%).

A comparison of the absorption spectra of solutions of pure $K_2[ReOHCl_5]$ with the known ones of Re(IV) solutions, obtained by reduction of $KReO_4$ with $SnCl_2$ [4], shows that the hydroxy-complex is a primary reduction product. It was confirmed that after a sufficiently long time, the absorption spectra of ReO_2 solutions in 6 M HCl are similar to those of the above mentioned binuclear complex, which is the last product of the reaction of ReO_2 with concentrated HCl at room temperature.

The hydroxy-complex changes successively into the binuclear complex:

$$2[ReOHCl_5]^{--} \rightleftharpoons [Re_2OCl_{10}]^{----} + H_2O.$$

At higher temperatures (above 30° C.) the equilibrium of this reaction is shifted towards the left, at lower temperatures (below 18° C.) — to the right. This behaviour may easily be confirmed by chemical reactions. μ-oxychlororhenate (IV) in combination with H_2O_2 gives an intense-red solu-

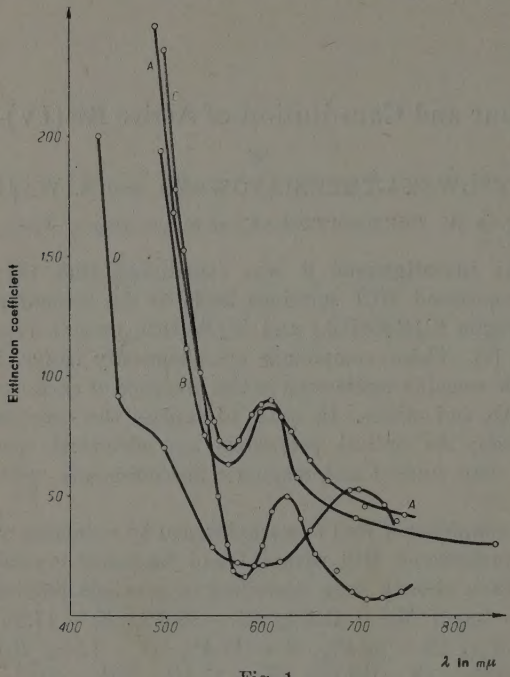

Fig. 1

A — Light absorption of $K_2[ReOHCl_5]$ in 2 M HCl
B — Light absorption of Re(IV) in 4 M HCl, according to Maun and Davidson [4]
C — Light absorption of $K_4[Re_2OCl_{10}]$ in 4 M HCl
D — Light absorption of ReO_2 in 6 M HCl, according to Maun and Davidson [4]

tion. It oxidises into perrhenate only after heating, whereas $K_2[ReOHCl_5]$ oxidises at once into a colour-less solution of Re(VII). Chinolin precipitates μ-oxychlororhenate (IV) which appears in the form of brilliant reddish-brown needles; chinolin hydroxy-chlororhenate (IV) is a bright brown, subcrystalline precipitate.

Measurements of the molar conductivities of 1/1000 M solutions of hydroxochlororhenate (IV) and μ-oxychlororhenate (IV) confirm the constitution of these compounds. The conductivity of the former is similar to that of a three-ionic salt ($\mu_M^{25°C.} = 220—240$), of the latter to that of a five-ionic salt ($\mu_M^{25°C.} = 500—540$).

The conductivity of these solutions changes with time. The hydroxychlororhenate (IV) solutions oxidise up to $KReO_4$ and consequently, the conductivity becomes constant after some hours:

$$2\,[ReOHCl_5]^{--} + 3/2\,O_2 + 3\,H_2O \rightarrow ReO_4^- + 10\,Cl^- + 8\,H^+.$$

μ-oxychlororhenate (IV) solutions undergo successive hydrolysis; the molar-conductivity rises continuously and after a few hours ReO_2 precipitates:

$$[Re_2OCl_{10}]^{----} + 3\,H_2O \rightarrow 2\,ReO_2 + 10\,Cl^- + 6\,H^+.$$

Magnetic measurements (by the Gouy method) of both active complexes showed that hydroxychlororhenate (IV) has a normal paramagnetism

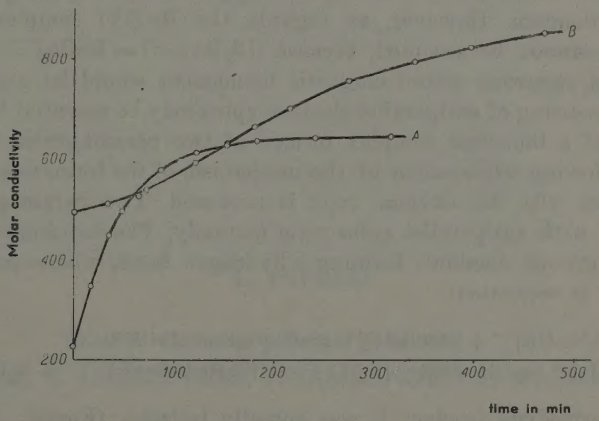

Fig. 2. *A* — $K_2[ReOHCl_5]$ *B* — $K_4[Re_2OCl_{10}]$

($\chi_M^{81°K} = 8120 \cdot 10^{-6}$, $\chi_M^{155°K} = 5640 \cdot 10^{-6}$, $\chi_M^{217°K} = 4540 \cdot 10^{-6}$, $\chi_M^{300°K} = 3580 \cdot 10^{-6}$) corresponding to a magnetic moment of 3.3 M. B. This indicates the presence of three unpaired electrons, as found by Klemm and Schüth [5] for the $K_2[ReCl_6]$ and $Ag_2[ReCl_6]$ ($\mu = 3.2$ M. B.). It can be assumed that the stability of chlororhenate (IV) results from the fact that there is an appreciable amount of the covalent bond. The substituting of one Cl by OH^- leads to an increase in the amount of ionic character of the bond. The μ-oxychlororhenate (IV) complex shows only a weak paramagnetism ($\chi_M^{160°K} = 379 \cdot 10^{-6}$, $\chi_M^{201.5K} = 344 \cdot 10^{-6}$, $\chi_M^{235°K} = 334 \cdot 10^{-6}$) which may be neglected, because it arises undoubtedly from factors other than electron spins, e. g. contamination with $K_2[ReOHCl_5]$, temperature-independent paramagnetism, etc. Therefore this compound may be considered as diamagnetic. The diamagnetism may be explained by the fact that the spins of the unpaired electrons of both Re atoms are mutually antiparallel, which leads to some electron pairing; nevertheless a direct bond between Re atoms, bounded by an oxygen atom, does not exist:

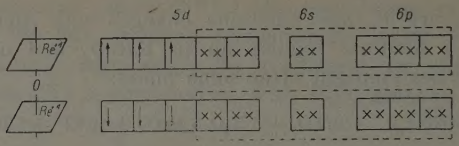

Fig. 3

A similar case of diamagnetic binuclear complex is to be found in potassium μ-oxychlororuthenate (IV) $K_4[Ru_2OCl_{10}]$ [6], [7]. Dunitz and Orgel [8] (and also Pauling) have suggested that the diamagnetism of this compound is explained by the formation of a double bond between the oxygen and ruthenium atoms $Ru=O=Ru$, the oxygen atoms requiring two d-orbitals of ruthenium. However, as regards the Re (IV) complex, such an explanation cannot be accepted, because $[Cl_5Re=O=ReCl_5]^{----}$ contains two unpaired electrons whose magnetic momement would be $\mu = 2.8$ M. B. Hence, some pairing of antiparallel-electron-spins may be essential for the diamagnetism of a binuclear complex formed of two paramagnetic metal-ions.

The following explanation of the mechanism of the formation of a binuclear complex with an oxygen bond is proposed. Two paramagnetic ions $[ReOHCl_5]^{--}$ with antiparallel spins react mutually. The coordinatively unsaturated OH groups combine, forming a hydrogen bond, whereupon a molecule of H_2O is separated:

$$[Cl_5Re\text{-}OH]^{--} + [HO\text{-}ReCl_5]^{--} \rightleftharpoons (I)\ [Cl_5Re\text{-}OH\colon OHReCl_5]^{----}$$
$$\rightleftharpoons (I)\ [Cl_5Re\text{-}OH\colon OHReCl_5]^{----} \rightleftharpoons (II)\ [Cl_5Re\text{-}O\text{-}ReCl_5]^{----} + H_2O.$$

Such an intermediate product (I) was actually isolated. (Found: Re-40.6%, Cl-38.6%; calc. Re-40.6%, Cl-38-6%). It is practically diamagnetic ($\chi_M^{216^0K} = 365 \cdot 10^{-6}$) and shows chemical properties corresponding to the hydroxy-complex, since in aequeous solutions it decomposes into two $[ReOHCl_5]^{--}$ ions.

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